# COAL-FIRED POWER MATERIALS

*Major advances in materials technology over the last decade have enabled building coal-fired power plants with much higher efficiencies than the current generation.*

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*Fig. 1 — View of a typical header. Headers are thick-walled extruded pipes in which the fluids carried by the tubes are mixed and homogenized. They serve either as receptacles(Inlet header) or dischargers(Outlet header.) Image courtesy Dr. F. Masuyama*

Very high-efficiency pulverized-coal power plants capable of operating at steam pressures and temperatures much higher than possible today are under development to provide relatively low-cost power with much less pollution.

Projects sponsored by the U.S. Department of Energy and the Ohio Coal Development Office have set 1400°F/5000 psi as the goal for what might be termed "Advanced UltraSuperCritical" (AUSC) coal-fired power plants. Europeans have carried out substantial research along the same lines under the AD 700 program. It is estimated that efficiency under these conditions will improve from 35% to nearly 46%, a 31% increase. This results not only in reduced fuel costs, but also in reduced balance-of-plant costs, due to less pulverizing, transportation, waste disposal, emission controls, and cooling-water consumption. It can also lead to a decrease in all waste products and emissions.

The major enabling technology for these AUSC plants is the availability of materials with high creep strength, corrosion resistance, and fabricability. This article reviews some of these alloys, with special reference to recent activities of a consortium of companies including Alstom Power, Babcock & Wilcox, Foster Wheeler, Riley Power, Electric Power Research Institute, Oak Ridge National Lab, and Energy Industries of Ohio. The consortium is under the sponsorship of the National Energy Technology Laboratory of the Department of Energy and the Ohio Coal Development Office.

**Boiler materials**

The function of a boiler is to convert water into superheated steam, which is then delivered to a steam turbine. Fuel with preheated air is burned in the furnace, which is constructed with a wall of welded tube panels known as the waterwall. The combustion gases flow through the furnace and evaporate the water into steam inside the furnace waterwall tubes. The steam is then further superheated in the superheater section, and delivered to the turbine via main steam pipes. The low-pressure steam exhausted from the high-pressure turbine is again reheated in a reheater section, and is delivered to the low-pressure turbines via the reheat pipes.

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The fluids in the system include combustion gases on the outside and water/steam on the inside of tubes and pipes.

The key components of a boiler carrying high-temperature, high-pressure steam can therefore be broadly classified into two configurations: tubes and thick-wall pipes. The pipes are generally known as headers or steam pipes, while the tubes are categorized into furnace-wall tubes and superheater/reheater tubes.

• **Headers:** An example of a header is shown in Fig. 1. It is a thick-wall pipe penetrated by a number of tubes. These heavy-section components have to meet creep strength and fatigue strength requirements based on thermal fatigue.

**Ferritic and martensitic steels** are preferred for this application because of their lower coefficient of thermal expansion and higher thermal conductivity compared to austenitic steels. Many of the early problems in the AUSC plants in thick-section austenitic steel components were traceable to their susceptibility to thermal fatigue.

Therefore, research during the last decade has focused on cost-effective, high-strength ferritic steels

## Table 1 — Bill of Materials for various components of Ultra Supercritical and Advanced Ultra Supercritical coal-fired power plant boiler steam conditions (1)

| Component | 1100°F/1100°F | 1150°F/1150°F | 1200°F/1200°F | 1300°F/1300°F (2) | 1350°F/1400°F (3) |
|---|---|---|---|---|---|
| SH Outlet Header/ Main steam pipe | P91, P92, E911 | P92, P122, E911, SAVE 12 | NF12, CCA617 | Nimonic263, CCA617 | IN740 |
| RH Outlet Header/RH pipe | P91, P92, E911 | P91, P92, E911 | Same as above | Nimonic263 | IN740 |
| SH panels (4) | Super304H, HR3C, 347HFG | Super304H, HR3C, 347HFG | NF 709, Cr 30A | Super304H, Sanicro25, HR3C, Super304H, 310N | IN617 347HFG |
| Finish SH (4) | Super 304H, HR3C, 347HFG | HR6W, HR120, HR3C | IN617 | IN617, IN740 | IN740 |
| Primary RH (4) | Super304H, HR3C, 347HFG | Super304H, H R3C, 347HFG | NF709, Cr 30A, Super304H | Sanicro 25, HR 3C, Super304H | 304H, 347HFG |
| Finish RH (4) | Super304H, HR3C, 347HFG | Super304H, HR3C, 47HFG | IN617 | IN617, IN740 | Haynes 230, Super304H, HR120 |
| Economizer | SA 210C | SA 210C | SA 210C | SA 210C | SA 210C |
| Lower waterwall | T11, T12, T22 | T22 | T22 | T23 | T23 |
| Upper waterwall | T 23, HCM12 | T23, HCM12 | HCM12, T23 | TI B1010, 7Cr Mo V T23, HCM12 | T92, HCM12 |

*1: Steam pressure of 4500 psi is assumed for this table; 2: Based on European AD700 Project; 3: Based on DOE/OCDO Project; 4: For corrosive, high sulfur /low NOx conditions SH/RH and waterwall tubes may require weld overlay or cladding with IN72 (42% Cr). Table 1 is for general information only, and does not include all the nuances considered by the designer. The service condition listed in each column represents the maximum conditions of exposure.*

## Table 2 — Candidate alloys for USC and AUSC plant boilers

| Alloy | Nominal Composition | Application | ASME Code |
|---|---|---|---|
| Haynes 230* | 57 Ni-22Cr-14W-2Mo-La | P, SH/RH Tubes | 2063 |
| INCO740* | 50Ni-25Cr-20Co-2Ti-2Nb-V-Al | P, SH/RHTubes | |
| CCA 617* | 55Ni-Cr-.3W-8Mo-11Co-Al | P, SH/RH Tubes | 1956 |
| HR6W* | 43Ni-23Cr-6W-NB-Ti-B | SH/RH Tubes | |
| Super304H* | 18Cr-8Ni-W-Nb-N | SH/RH Tubes | |
| Save12* | 12Cr-W-Co-V-Nb-N | P | |
| NF 616 (P-92) | 9Cr-2W-Mo-V-Nb-N | WW Tubes | 2179 |
| HCM2S (P-23) | 2-1/4Cr-1.5W-V | WW Tubes | 2199 |
| HCM12 | 12Cr-1Mo-1W-V-Nb | WW Tubes | |
| 347HFG | 18Cr-10Ni-Nb | SH/RH Tubes | 2159 |
| NF 709 | 20Cr-25Ni-NB-Ti-N | SH/RH Tubes | |
| HR3C | 25Cr-20Ni-Nb-N | SH/RH Tubes | 2113 |
| HCM12A (P122) | 12Cr-1.5W-Mo-V-Nb_N | P | 2180 |
| NF12 | 11Cr-2.6W-2.5Co-V-Nb-N | P | |
| IN625 | 21.5Cr-9Mo-5Fe-3.6Nb-AI-Ti | P, T | 1409 |
| HR120 | Ni-33Fe-25Cr-N | T | 2315 |
| E911 | 9Cr-1Mo-1W-V-Nb-N | P | |
| Sanicro25 | 22Cr-25Ni-3.5W-3Cu-Nb-N | | |

** Alloys studied in the DOE/OCDO Project; P-Pipe; SH - Superheater; RH - Reheater; WW - Waterwall*

that could help avoid austenitic stainless steels in heavy-section components. This has resulted in ferritic steels capable of operating at metal temperatures up to 620°C (1150°F), with good weldability and fracture toughness. **Nickel-base alloys** are chosen for higher temperatures, thus bypassing the need for austenitic stainless steel components.

• **Tubes:** For tubing applications, thermal fatigue is not a key issue because of the smaller section size.

**Austenitic steels** are suitable up to about 1250°F (680°C). However, **nickel-base alloys** are needed at higher temperatures, because they provide more creep resistance. Developments are also underway to extend the limiting temperature for austenitic steels as a cost-effective means of replacing the nickel tubing. A sample list of boiler materials for plants operating with various steam conditions is provided in Table 1. The basic compositions of the alloys are shown in Table 2.

In addition to creep strength, resistance is needed to hot corrosion from the fireside, and to oxidation corrosion from the steam-side of tubes. Fireside corrosion can lead to premature failures due to the increase in stresses caused by reduced cross section.

Steam-side oxidation promotes accelerated creep due to reduction of cross section, progressive increase in tube metal temperature, and blockage of tubes by spalled oxides. In addition, it causes erosion of turbine steam path components by exfoliated oxide particles. To minimize

corrosion while keeping costs down, austenitic steel tubes serve in the SH/RH portions of the boiler.

Property requirements for waterwall tubes are similar, with the caveat that the fireside corrosion mechanisms are somewhat different. Since the temperatures are lower than for superheaters, ferritic steels with claddings or coatings possess adequate creep strength and corrosion resistance.

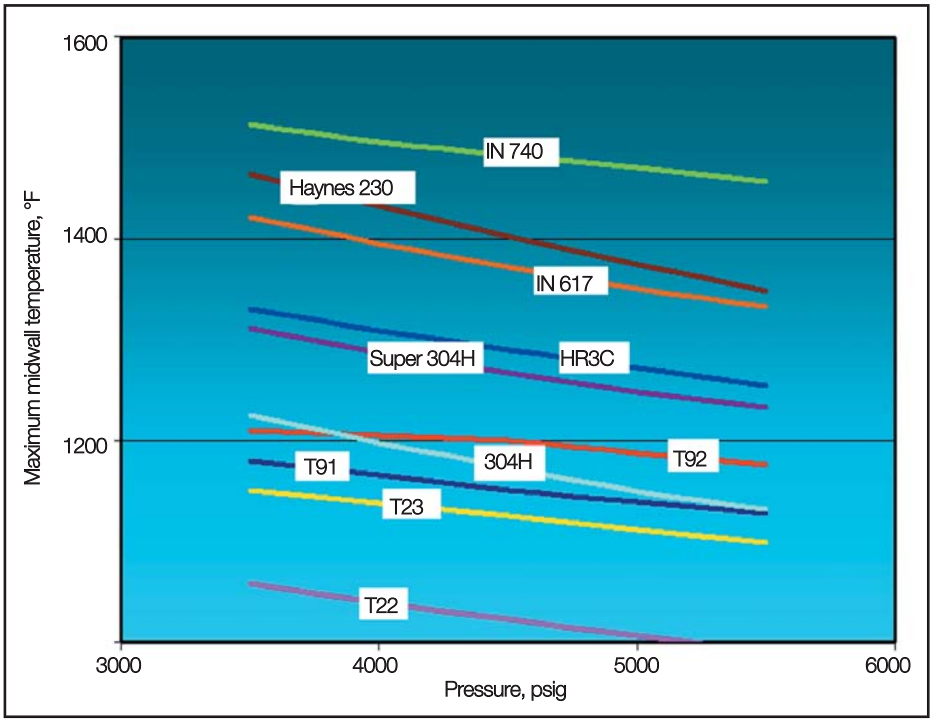


*Fig. 2 — Maximum usage pressure/temperature. The best ferritic steel can go up to 620°C (1150°F). Developmental ferritics can reach 650°C (1200°F), austenitics can function up to 675°C (1250°F), and nickel alloys function above that, purely based on creep strength. Courtesy of Steve Goodstine, Alstom.*

**Advanced alloys for 760°C (1400°F)**

In the high-temperature and stress environment envisaged for the AUSC steam boiler, the limiting mechanical material property is long-term creep strength. A general criterion of an average stress of 100 MPa (14.5 ksi) to produce rupture in 100,000 hours can serve as a guideline to set the temperature or stress limits. Based on the creep strength criterion, the program selected six advanced alloys as candidate materials for the target plant of 1400°F (760°C)/5000 psi (35 MPa) steam conditions.

Basic compositions of the candidate alloys are included in Table 2. Nickel-base alloy Haynes 230, Inco 740, and CCA 617 were selected for heavy section, high-temperature headers, pipes, and SH/RH tubing.

• **The austenitic steels** HR 6W and Super 304H Steel were considered for high-temperature tubing; and the ferritic steel SAVE 12 was selected as a candidate for both applications at lower temperatures. Figure 2 includes the stress ranges for the alloy classes and shows that for temperatures above ~700°C (1290°F), age hardenable alloys (Inconel 740 shown) and Haynes 230 will be necessary to meet the 100 MPa criteria.

In support of the U.S. program, extensive long-term creep-rupture testing (now beyond 38,000 hours) is being conducted by Oak Ridge National Laboratory to understand how creep performance is affected by microstructural changes, heat-to-heat material variability, fabrication processes, and welding.

Utilizing the findings of these studies, the consortium is gaining confidence in the performance of new materials, and is providing the groundwork for the development of ASME stress allowables, developing improved fabrication rules, and determining the applicability of weld materials/processes. Microstructural characterization, material modeling, and computational thermodynamics are key tools in the evaluation process.

In addition to the creep strength of the base metal, strength of the welds is also a major determining factor. Weld-strength reduction factor (WSF) is defined as the ratio of the stress-to-rupture of the welded joint, to the stress-to-rupture of the base metal for a given time and temperature. For a number of candidate AUSC nickel-base alloys (including Haynes 230), the weld metal is the weakest link, and it fails at a shorter time interval or lower stress level than the base metal.

In the case of Haynes 230, the weld strength factor has not been found to be a strong function of testing time, so a general WSF of 0.8 is appropriate, which should not be a hindrance to current boiler design of component welds. However, for other AUSC materials, data indicate lower WSF. Therefore, research is ongoing to improve weld performance through changes to weld processes, filler metal chemistry, and post-weld heat treatment.

Another consideration for boiler materials is that cold strain due to fabrication processes (bending, swaging, etc.), may cause a degradation in creep strength. To understand this phenomenon, full-scale pressurized creep tests are being conducted on cold-bent boiler tubes (two inches O.D., 0.4-inch wall thickness) in the as-bent condition and in the heat-treated condition.

After one year of testing on a nickel-base alloy, metallographic examination revealed extensive creep damage (cavitation) and some recrystallization in a highly strained tube bend. However, a second bend with slightly less cold strain had no creep damage even at 1/3 life. These data serve as the basis to set rational cold-work limits for the guidelines in the ASME B&PV Code.

In addition to creep strength considerations, the project consortium has also extensively evaluated the steamside oxidation, fireside corrosion, and fabricability of the alloys selected for AUSC plant boilers. These studies will be discussed in Part 2 of this paper next month. Review of turbine materials will be included in a future issue.


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